

## AMENDED SPECIFICATION

Reprinted as amended in accordance with the Decision of the Superintending Examiner  
acting for the Comptroller General dated the first day of September, 1966, under  
Section 29, of the Patents Act, 1949.

## PATENT SPECIFICATION

978,853



NO DRAWINGS

978,853

Inventors: LOUIS OTTO RAETHER  
and ALBERT JOHN LAUCK

Date of Application and filing Complete Specification: April 4, 1961.  
No. 11952/61.

Complete Specification Published: Dec. 23, 1964.

© Crown Copyright 1964.

Index at acceptance:—C2 C(3A10E4A3, 3A10E4C, 3A10E5F1A, 3A10E5F2A, 3A10E5F2B,  
3A10E5F3C, 3A10E5F3D); C3 P(10C20D1, 10C20D2, 10C20D3, 10D1A,  
10D2A, 10K4, 10K7, 10K8, 10K9)

International Classification:—C07c (C08f)

## COMPLETE SPECIFICATION

## Esters and Compositions containing the same

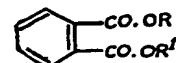
We, MONSANTO COMPANY, previously known as Monsanto Chemical Company, a corporation organised under the laws of the State of Delaware, United States of America, of 800 5 North Lindbergh Boulevard, St. Louis, 66, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to esters of phthalic acid, to the production thereof and to vinylidene halide polymers plasticised therewith.

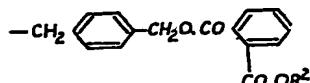
15 There is an insistent demand for plasticisers for vinylidene halide polymers which are of very low volatility and which are extracted with difficulty from the compositions in which they are present. Compositions which have been plasticised with plasticisers 20 which are deficient in these properties are liable to become brittle, to shrink and so lose their usefulness. Examples of uses of plasticised vinylidene halide polymers in which such plasticisers are required are upholstery 25 materials, leather substitutes used for shoe making and the translucent roofs of road vehicles.

30 The object of the invention is to provide plasticisers which possess both low volatility and are difficultly extractable with petroleum hydrocarbons.

According to the present invention there 35 is provided an ester of phthalic acid having the general formula



in which R is an alkyl group and R' is a cycloalkyl group having a six-membered ring or a group having the general formula



40

45

50

55

55

60

in which R<sup>2</sup> is an alkyl group, the total number of carbon atoms in R and R' being at least 12 and when R' is a cycloalkyl group R either has fourteen carbon atoms or is derived from catalytically hydrogenated coconut oil alcohols.

The esters of the present invention fall into two sub-groups depending upon the nature of the second esterifying group. In all cases one of the carboxyl groups of phthalic acid is esterified by an alkanol. In one sub-group of the esters the second esterifying group is a cyclohexyl group whilst in the other sub-group it is a para-xylylene group which is used to esterify two alkyl acid phthalate groups.

In the first sub-group appropriate alkyl acid phthalates may be esterified with a cyclohexanol, more especially with cyclohexanol or a methylcyclohexanol, or, alternatively a cyclohexyl acid phthalate may be esterified

BEST AVAILABLE COPY

with an appropriate alkanol. The esterification may conveniently be carried out by heating a cycloalkyl acid phthalate and the alkanol in the presence of a conventional esterification catalyst such as a toluene sulphonic acid.

In the second sub-group alkyl acid phthalates are most conveniently esterified with an  $\alpha,\alpha'$ -dihalo-para-xylene in the presence of an acid acceptor. It is most convenient to use  $\alpha,\alpha'$ -dichloro-para-xylene as the  $\alpha,\alpha'$ -dihalo-para-xylene. The acid acceptor is preferably a tertiary amine and may be a tertiary alkylamine. This method of esterification is much more convenient than that which would require the intermediate preparation of para-dimethylolbenzene.

The acid phthalates used in the process of the invention may be produced *in situ* by the reaction between phthalic anhydride and the alkanol or cycloalkanol. The alkanols or cycloalkanols used may be pure individuals or mixtures. Thus where appropriate the mixture of alkanols may be one of decyl or tri-decyl alcohols obtained by the "oxo" reaction on propylene trimer or tetramer, carbon monoxide and hydrogen or by the catalytic hydrogenation of coconut oil (containing approximately 60% of *n*-octanol, 33% of *n*-decanol, 5% of *n*-hexanol and 0.6% of *n*-dodecanol).

The esters of the present invention are very valuable permanent plasticisers for vinylidene halide polymers and are markedly superior to diethyl phthalate in this respect. The esters have an extremely high degree of stability against exudation from compositions containing such esters and vinylidene halide polymers. They are not readily extracted by hydrocarbons and vinylidene halide polymer compositions containing them retain their flexibility at low temperatures.

The term "vinylidene halide polymer" is intended to include homopolymers of vinyl chloride and vinylidene chloride, and copolymers of vinyl chloride and vinylidene chloride with other ethylenically unsaturated monomers copolymerisable therewith, such as copolymers of vinyl chloride and vinylidene chloride with vinyl esters of carboxylic acids, e.g., vinyl acetate, vinyl propionate, vinyl butyrate and vinyl benzoate; with esters of ethylenically unsaturated acids, e.g. alkyl acrylates such as methyl, ethyl, propyl and butyl acrylates and the corresponding esters of methacrylic and ethacrylic acids; with vinyl aromatic compounds, e.g. styrene, ortho- and para-chloro styrene, the dichloro styrenes such as 2,5-dichloro styrene, divinyl benzene, vinyl naphthalene and  $\alpha$ -methyl styrene; with ethylenically unsaturated amides, e.g. acrylic acid amide and acrylic acid anilide; with ethylenically unsaturated nitriles, e.g. acrylonitrile and methacrylonitrile; and with esters

of  $\alpha,\beta$ -ethylenically unsaturated dicarboxylic acids, e.g. the methyl, ethyl, propyl, butyl, tert-butyl, amyl, hexyl, octyl, decyl, dodecyl, tridecyl, allyl, methallyl, phenyl alkyl and phenalkyl monoesters and diesters of maleic, itaconic and fumaric acids. Such copolymers should contain at least 50% by weight and preferably at least 70% by weight of a vinyl or vinylidene halide. Preferred polymers are those in which substantially 70% by weight of the monomer units are vinyl chloride units, any balance being monomer units derived from an ethylenically unsaturated monomer.

Similar polymers and copolymers in which the vinylidene chloride or vinyl chloride is partly or wholly replaced by other vinylidene halides may also be used. Such vinylidene halides may be vinyl bromide, vinylidene bromide and vinyl fluoride.

Although the quantity of plasticiser used will depend upon the particular polymer or copolymer to be plasticised and its intended use, compositions containing from 25 to 300 parts of plasticiser per 100 parts of polymer can be used since the esters may be used for making rigid plastic products as well as flexible products, e.g. plastisols. Such quantities of the plasticisers are herein termed "plasticising amounts."

The following examples illustrate the preparation of the esters of the invention. All parts are parts by weight.

#### EXAMPLE 1

A suitable reaction vessel fitted with a reflux condenser and an agitator was charged with 148.1 parts of phthalic anhydride and 100 parts of cyclohexanol. The resulting mixture was heated for 30 minutes at temperatures not exceeding 130°C. thus forming cyclohexyl acid phthalate, 310 parts of tri-decanols prepared by the "Oxo" process, 5 parts of toluene sulphonic acid and 1 part charcoal were then charged to the reaction mixture and the resulting mixture heated for 3 hours at temperatures of 75 to 125°C. and from 35 to 760 mm. of mercury absolute pressure while removing water evolved during the reaction. Thereafter, the reaction mass was filtered, successively washed with sodium carbonate solution and water, steamed and dried to yield cyclohexyl "Oxo"-tridecyl phthalate, a colourless liquid which is very viscous at room temperature, having an index of refraction,  $n_{D}^{25}$ , of 1.4950 and a specific gravity at 25°C/25°C. of 0.996.

The above experiment is not an example of the invention, but in, a similar manner other alkyl cyclohexyl phthalates, including those in which the alkyl group is *n*-tetradecyl, are similarly prepared. One of these esters and its physical properties are tabulated below.

Compound	Colour and State	$n_d^{25}$	Sp. Gr. at 25° C./25° C.
*Mixed <i>n</i> -Decyl, <i>n</i> -Octyl cyclohexyl phthalate	Colourless liquid	1.4954	1.0157

\* Prepared from a mixture of alcohols derived from coconut oil by the hydrogenation thereof and containing approximately, by weight, 60% of *n*-octanol, 33% of *n*-decanol, 5% of *n*-hexanol, 0.6% of *n*-dodecanol and the remainder hydrocarbons.

**EXAMPLE 2**

A suitable reaction vessel fitted with an agitator is charged with 81.4 parts of phthalic anhydride, 72.3 parts of 2-ethylhexanol, 55.6

parts of triethylamine, 43.8 parts of  $\alpha\alpha'$ -dichloro-para-xylene and 50 ml. of toluene in the following manner:

Time Minutes	Temperature °C.	Remarks
0	27	Phthalic anhydride, alcohol and a few drops of amine in vessel. Heat turned on
14	108	Heat off. Reaction mass is clear
30	123	Heat still off
90	43	Add dichloro-para-xylene. Start adding amine. An exothermic reaction ensues
92	74	All amine added
95	76	Heat turned on
110	91	Heat off
120	135	Reaction mass very viscous
121	134	Add 50 ml. of toluene
122	119	Heat turned on
127	125	Reaction mixture stirred
157	125	Heat off. Reaction complete

10 The reaction mass is washed three times at 60°C. to 70°C. The first wash is with 250 ml. of water containing 3 ml. of concentrated hydrochloric acid, the second wash with 250 ml. of water containing salt and the third wash it with a lye solution which is just sufficiently alkaline to give a pink colour to phenolphthalein. A final wash with water was then given. The organic material remaining after the washing operation is steamed at 110° to 120°C./200 mm. of mercury absolute pressure for 45 minutes to remove toluene, excess alcohol and other impurities. The product is then washed once with 250 ml. of water containing 1 ml. of 50% lye and three more times with 250 ml. portions of water. After drying at 110° to 115°C./35 mm. of mercury absolute pressure for 15 minutes and filtering, there remains substantially 130 parts of para-phenylenedimethylene bis(2-ethylhexyl phthalate), a colourless liquid having a viscosity of 27 poises at 25°C. and a specific gravity of 1.097. 25

15 In a similar manner other para-phenylenedimethylene bis(alkyl phthalates) may be similarly prepared, including those in which the alkyl groups are methyl, ethyl, *n*-propyl, *isopropyl*, *n*-butyl, *iso*-butyl, *tertiary*-butyl, *amyl*, *n*-hexyl, *dimethyl*-butyl, *heptyl*, *octyl* *nonyl*, *decyl*, *dodecyl*, *tridecyl*, *pentadecyl* and *octa*- 30

20

5 decyl. The two alkyl groups present in the esters may be like or unlike. Preferably each of the alkyl groups has at least four carbon atoms. There may thus be prepared such compounds as para - phenylenedimethylene bis(methyl phthalate), para - phenylenedimethylene bis(*n*-butyl phthalate) a colourless liquid having an index of refraction at 25°C. of 1.5455, a specific gravity at 25°/25°C. of 10 1.162 and a viscosity at 25°C. of 18 poises, paraphenylenedimethylene bis(phthalate) of catalytically hydrogenated coconut oil alcohols, a colourless liquid having a specific gravity at 25°C. of 1.081 and a viscosity of 6 poises at 15 25°C., para-phenylenedimethylene bis("Oxo" - decyl phthalate) a colourless liquid having a specific gravity of 1.076 at 25°C. and a viscosity of 27 poises at 25°C., and para-phenylenedimethylene bis("Oxo" - tridecyl phthalate). The decyl groups in the para-phenylenedimethylene bis("Oxo" - decyl phthalate) are those of a mixture of primary decyl alcohol prepared by the "Oxo" process which mixture is of branched chain primary 20 25 alcohols comprising dimethyloctanols and trimethylheptanols having a methyl group in the 3-position.

In order to demonstrate the outstanding permanence of vinylidene halide resin compositions containing the alkyl cyclohexyl phthalates comparative tests were made using polyvinyl chloride resin compositions in which the plasticisers were either the alkyl cyclohexyl phthalates or known dialkyl phthalates. The latter were chosen because of their chemical similarity to the alkyl cyclohexyl phthalates and because of their widespread use as plasticisers for vinylidene halide polymer resins. In addition to comparing the properties affecting permanence, i.e. volatility and extraction by hydrocarbons, the low temperature properties of the plasticised compositions were also compared. Test samples were prepared using 40 parts by weight of plasticiser for each 100 parts of polyvinyl chloride resin. The volatility of the plasticiser was determined using Method D1203-52T, ASTM Standards on Plastics, March 1953, page 795, the resistance to hydrocarbon extraction using Method D543-52T, *loc. cit.*, page 785, and the low temperature flexibility point by Method D1043-51, ASTM Standards on Plastics, September 1958, page 305. The following results were obtained:

Plasticiser	Volatility % Plasticiser lost	Extraction % Plasticiser lost	Low Temperature Flexibility Point, °C.
Di-hexyl phthalate	18.2	8.2	-30
Di-octyl phthalate	14.8	8.0	-37
Di-decyl phthalate	1.9	8.7	-35
Mixed Di( <i>n</i> -Decyl, <i>n</i> -Octyl) phthalate (as described above)	1.9	8.6	-46
<i>n</i> -Tetradecyl cyclo- hexyl phthalate	1.1	8.0	-20
Mixed ( <i>n</i> -Decyl, <i>n</i> -Octyl) cyclohexyl phthalate (as described earlier)	3.4	4.7	-28

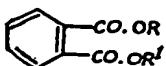
60 It is evident from the above table that the alkyl cyclohexyl phthalates provide outstandingly permanent plasticised vinylidene halide polymer compositions and are far superior even to dioctyl phthalate, the standard plasticiser used in the industry. Hitherto adequate permanence with respect to both volatility and kerosene extraction could not be obtained by the use of a single plasticising ester. It is now possible to secure both of 65 these desirable properties by the use of a single plasticising ester as well as desired low temperature flexibility.

The esters containing a para-phenylenedimethylene group are outstanding as permanent plasticisers for the vinylidene halide polymer resins particularly with respect to their extremely high degree of stability against exudation under conditions of high humidity, a property generally not exhibited by the so-called permanent or polymeric plasticisers. In this respect two compounds of this invention are particularly outstanding, namely, para-phenylenedimethylene bis(phthalate) of catalytically hydrogenated coconut oil alcohols and para-phenylenedimethylene bis("Oxo" - decyl

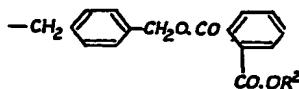
phthalate). A sheet was prepared using each of these compounds by milling 40 parts by weight of the ester with 100 parts of poly-vinyl chloride. Each sheet was then placed in a testing device in which the temperature was 60°C. and the relative humidity was 100 percent. After 25 weeks under such conditions no evidence of exudation of the plasticiser could be detected. In contrast thereto compositions in which known commercial polyester plasticisers are used usually show evidence of exudation after 1 to 10 weeks under the same conditions of temperature and humidity.

15 WHAT WE CLAIM IS:—

1. An ester of phthalic acid having the general formula



20 in which R is an alkyl group and R<sup>1</sup> is a cycloalkyl group having a six-membered ring or a group having the general formula



25 in which R<sup>2</sup> is an alkyl group, the total number of carbon atoms in R and R<sup>1</sup> being at least 12 and when R<sup>1</sup> is a cycloalkyl group R either has fourteen carbon atoms or is derived from catalytically hydrogenated coconut oil alcohols.

30 2. n-Tetradecyl cyclohexyl phthalate.  
 3. The cyclohexyl phthalate of catalytically hydrogenated coconut oil alcohols.  
 4. A para-phenylenedimethylene bis(alkyl phthalate) in which each of the alkyl groups has at least four carbon atoms.  
 35 5. Para-phenylenedimethylene bis(2-ethylhexyl phthalate).

6. Para - phenylenedimethylene bis(n-butyl phthalate).  
 7. Para-phenylenedimethylene bis("Oxo"-decyl phthalate).  
 8. The para - phenylenedimethylene bis(phthalate) of catalytically hydrogenated coconut oil alcohols.  
 9. A process for producing an alkyl cycloalkyl phthalate as claimed in any of claims 1 to 3 which comprises heating a cyclohexyl acid phthalate with an appropriate alkanol in the presence of an esterification catalyst.  
 10. A process according to claim 9 in which the cyclohexyl acid phthalate is cyclohexyl acid phthalate and the alkanol has 14 carbon atoms.  
 11. A process for producing a para-phenylenedimethylene bis(alkyl phthalate) which comprises heating an  $\alpha\alpha'$ -dihalo-para-xylene with an alkyl acid phthalate in the presence of an acid acceptor.  
 12. A process according to claim 11 in which the  $\alpha\alpha'$ -dihaloxylenes is  $\alpha\alpha'$ -dichloro-para-xylene.  
 13. A process according to either of claims 11 and 12 in which the acid acceptor is a tertiary amine.  
 14. A process according to claim 13 in which the tertiary amine is a tertiary alkyl-amine.

15. A composition comprising a polymer of a vinyl halide or a vinylidene halide and at least sufficient of an ester according to any of claims 1 to 8 to exert a plasticising action thereon.

16. A composition according to claim 15 in which the vinyl halide polymer is polyvinyl chloride.

17. A composition according to claim 15 in which the vinyl halide or vinylidene halide copolymer contains at least 70% by weight of vinyl or vinylidene halide.

STEVENS, LANGNER, PARRY  
& ROLLINSON,  
Chartered Patent Agents,  
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.

**THIS PAGE BLANK (USPTO)**